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SENSITIVITY FUNDAMENTALS.

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ABSTRACT

The failure diameter and shock sensitivity of 2, 2-DP were measured in lead tubes of 1-mm wall thickness and of IBA in tubes of 1.5-mm wall. The failure diameter of 2, 2-DP is less than 5 mm. In 9.5 mm I. D. x 2 mm wall cups the sensitivity is 87 ± 6 kbars. The diameter in which IBA propagates a detonation lies between 10 and 15 mm in 1.5-mm wall tubes. In 20 mm I. D. x 2 mm wall cups the sensitivity is 75 ± 6 kbars.

We are developing a test to be useful as a standard method for measuring sensitivity of liquids at extremes of temperature and pressure. The criterion for detonation is the measurement obtained for shock velocity. Two techniques are being explored: electronic and explosive witness. Preliminary experiments with the latter indicate that a modified Dautriche method can be used at ambient and cryogenic temperatures to measure detonation velocity and, therefore, detonability.

In lead confinement, the failure diameter of 1, 2-DP and 2, 2-DP was found to be less than 0.8 mm; that of IBA was 0.8 mm according to the work so far completed. This general range of failure diameters corresponds, under the assumptions made in the theory of failure diameter of homogeneous materials, to frequency factors between 10^{14} and 10^{15} sec^{-1}, and activation energies between 25 and 35 kcal/mole in the expression for the temperature variation of the first-order reaction constant.

Decomposition of 1, 2-DP in methanol is accelerated by HCl and LiCl to about the same extent; $LiClO_4$ also shows catalytic activity. The data suggest that anionic rather than acid catalysis is an important mechanism for catalyzed elimination of HF from difluoroaminopropanes. 1, 3-DP decomposes at 176-200° by HF elimination giving a small amount of malononitrile and a major amount of nonvolatile residue. Chloroacetic acid catalyzes this decomposition at 176° markedly in nitrobenzene and weakly in chlorobenzene.

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I INTRODUCTION

The previous report[1] on the Stanford Research Institute program concerning the fundamental sensitivity properties of difluoroamino compounds reviewed and discussed the experimental information obtained with respect to thermal stability, detonability, and decomposition kinetics of several bis(difluoroamino)propane isomers and IBA. Specifically the program was divided into four interrelated parts:

(a) The shock sensitivity to detonation of the liquid phase

(b) The relation of shock sensitivity and failure diameter to the flow and chemical reaction rate behind the shock front

(c) The adiabatic self-heating of the liquid phase

(d) The mechanism and kinetics of thermal decomposition.

Beginning with this quarter the program is being modified and expanded to include new tasks relating to detonation and thermal decomposition phenomena. The detonation studies will include (a) measurement of the shock sensitivity of the difluoroamino compounds of interest; (b) determination of whether or not the compounds exhibit low-order detonation and, if so, the necessary conditions for initiation, (c) modification of the JANAF sensitivity test so that it will be more meaningful and adaptable to conditions of extreme temperature and pressure.

The theoretical study will include adjunctive experimental studies in the physics and chemistry of detonation. The objectives of this phase of the work are (a) to demonstrate the steady detonation of difluoroamino compounds (b) to establish failure diameters of difluoroamino compounds in metals and other materials, (c) to study events in the liquids as shocks of various magnitudes enter (d) to study, where possible, the Chapman-Jouguet velocity, equation of state of the unreacted materials, and the divergence of the reacting material in the wave.

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[1] SRI Technical Progress Report No. 64-2, Annual, "Relationship Between Decomposition Kinetics and Sensitivity," March 15, 1963, to March 14, 1964 Contract Nonr 3760(00)

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The study of the kinetics and mechanisms of thermal decomposition of difluoroamino compounds will continue along lines previously established and will include, in addition, a study of the effect of acidic, basic, or neutral additives on their decomposition.

This quarterly report reviews the initial work on the modified JANAF sensitivity test, and the recent results from studies of detoration sensitivity, failure diameter, and decomposition of 1,2- and 2,2-bis-(difluoroamino)propane (1,2- and 2,2-DP) and 1,2-bis(difluoroamino)-2 methyl propane (IBA), the decomposition of 1,3-bis(difluoroamino)propane was also studied.

II DETONATION SENSITIVITY

(A. E. Amster, D. M. McEachern, Jr.)

The shock sensitivities of 2,2-DP and IBA have been measured using plastic attenuators and the CRISP apparatus to detect detonation.[1] In one experiment the failure diameter of 2,2-DP was found to be less than 5 mm in unslotted 1-mm-wall lead cups. Sensitivity was measured in 9.5 mm I.D. lead cups with 2-mm walls. Table I summarizes these results.

Table I

SHOCK SENSITIVITY OF 2,2-DP

Shot #	Gap (inches)	Gap (mm)	Result
10298-1	Zero	0	Go
10298-2	0.55	14.0	No go
10296	0.46	11.6	Go
10325-1	0.50	12.7	Go
10325-2	0.54	13.7	No go

The measured sensitivity is thus 0.52 ± 0.02 inch or 87 ± 6 kbars initiation pressure.

Using cups of different diameters, the failure diameter of IBA was found to lie between 10 and 15 mm in 2-mm-wall lead tubes and testing was done in 20 mm I.D. x 2 mm wall lead cups. The results (Table II) indicate that the sensitivity of IBA is $0.56_5 \pm 0.01$ inch of plastic or 75 ± 6 kbars.

Future plans are to conduct additional shock velocity measurements in Plexiglas attenuators with the booster used in the sensitivity tests in order to define better the initiation pressure. Also the effect upon apparent sensitivity of replacing the "flowerpot" plane wave generator with a tetryl pellet will be studied, using standard acceptors such as tetryl, Composition B, and nitromethane.

Table II

SHOCK SENSITIVITY OF IBA

Shot #	Gap (inches)	Gap (mm)	Result
10327-1	0.50	12.7	Go
10327-2	0.75	19.0	No Go
10327-3	0.62	15.7	No Go
10327-4	0.56	14.2	Go
10327-5	0.59	15.0	No Go
10327-6	0.57	14.4	No Go

In addition, we will repeat the sensitivity tests on 1,2-DP in a larger diameter to study the shape of the diameter-sensitivity curve.

III ADAPTATION OF THE JANAF BOOSTER TEST

(A. B. Amster, D. B. Moore, and J. Berke)

A. Introduction

High energy liquids are often exposed to conditions, such as extremes of temperature, which may change their susceptibility to shock initiation. Moreover, certain high energy materials are liquid only at extreme conditions of temperature and pressure. There exists a need for a detonation sensitivity test applicable to these situations. This is the first report on a program to adapt the current JANAF test for use under the following conditions:

$$77^{\circ}K < T < 373^{\circ}K$$

$$1 \text{ atm} < P < 10 \text{ atm}$$

An important aspect of the test where modification and improvement are indicated is the method of establishing whether detonation has occurred. The present test prescribes the use of a witness plate, but it is becoming apparent that such damage criteria are of limited value even at ambient conditions. Furthermore, experience at liquid nitrogen temperatures indicates that the witness plate and confining tube become so brittle as to render them valueless when so used. A test method for use at extremes of temperature or pressure or both would require additional packaging (as distinguished from confinement) within which to control the environment. It would not appear profitable to pursue a search for a transparent package through which optical measurements might be obtained. Thus the test should be modified so that detonation is detected and confirmed by velocity rather than damage criteria--the velocity being measured by non-optical means.

One of the simplest and most reliable methods for measuring detonation velocity is that developed by Dautriche. An adaptation of the technique, shown schematically in Fig. 1, can yield results of a high degree of reliability and adequate precision while at the same time retaining considerable simplicity. The detonation detector is detonating

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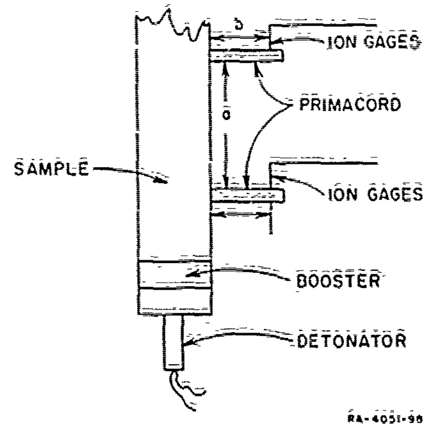

FIG. 1 DETONATION VELOCITY APPARATUS

cord either directly in contact with the sample or separated from it by a thin membrane. When sample detonation initiates the cord, the ion gauges are activated, the time of activation being recorded oscillographically. Knowledge of the detonation velocity of the cord and of the values of the distances a and b permits determination of the detonation velocity of the sample. The success of the method depends upon the reliability with which the cord is initiated by the acceptor. A similar arrangement which does not require the use of oscilloscopes will be described later. Two other methods are also available for the measurement of detonation velocity: ionization probes and continuous wire. We have tried the former at cryogenic temperatures and have experienced some difficulty, perhaps attributable to interactions between probes and confinement.

The continuous wire, as reported elsewhere, has performed reliably with some liquids at cryogenic temperatures; additional measurements might profitably be made to establish the conditions under which it is reliable.

The design of a test geometry for use at cryogenic temperatures and ambient pressure should prove to be straightforward. Emphasis should be placed upon the development of a test which is simple to

assemble and perform. Components should be readily available or inexpensive to manufacture and should be interchangeable. The requirements of a test at high temperature and high pressure differ from those at cryogenic temperature and ambient pressure. It may therefore be necessary to provide for interchangeable modules useful under different circumstances.

In the development of a broadly applicable test the order of tasks to be undertaken will be:

1. Evaluation of velocity measurement techniques at
   a. Ambient and high temperatures
   b. Cryogenic temperatures
2. Definition of the limits of applicability and reliability of each method
3. Design and testing of a suitable package unit or, if necessary, units
4. Integration of the sensor within the package
5. Modification of the package, where possible, to make the test inexpensive and simple
6. Demonstration of the test usefulness by measuring the detonability of sample liquids such as: N_2F_4, CH_3NO_2, and TNT.

B. Experimental Program

The first experiments were designed to develop a test for use where electrical power is unavailable. The method, shown schematically in Fig. 2, is an elaboration of the Dautriche method in which the detonation velocity in a known material is compared with that in the sample under study. The tetryl initiates the detonating fuse, which in turn initiates the explosive sheet at the "start" position. This detonation propagates further along each "finger" of the explosive sheet.

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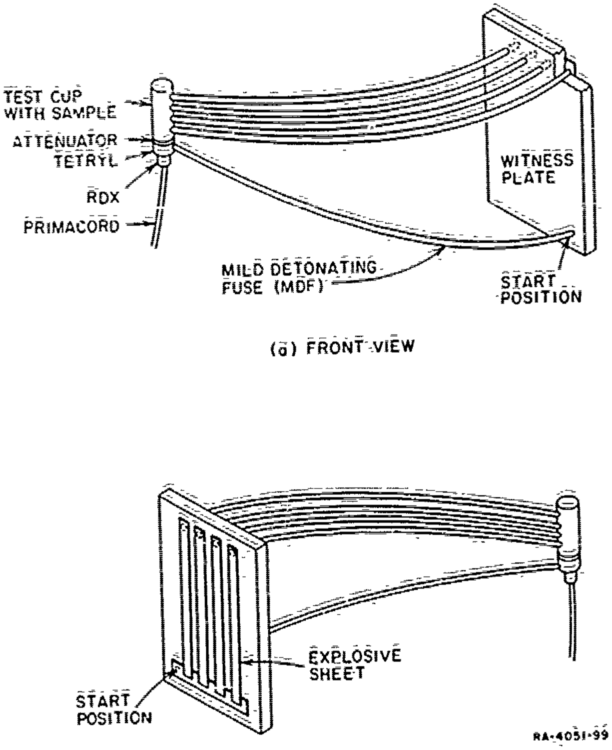


(a) FRONT VIEW

(b) REAR VIEW

FIG. 2 TEST ARRANGEMENT

A strong wave in the sample will also initiate the remaining pieces of fuse in order. Where the detonation waves collide within the fingers, dents are created in the witness plate deeper than those left by a unidirectional wave. The result of a typical shot is shown in Fig. 3. From the position of the dents and the properties of the system, the wave velocity within the sample can be calculated (see Appendix). For detonating samples at ambient temperature and pressure this method is known to work.

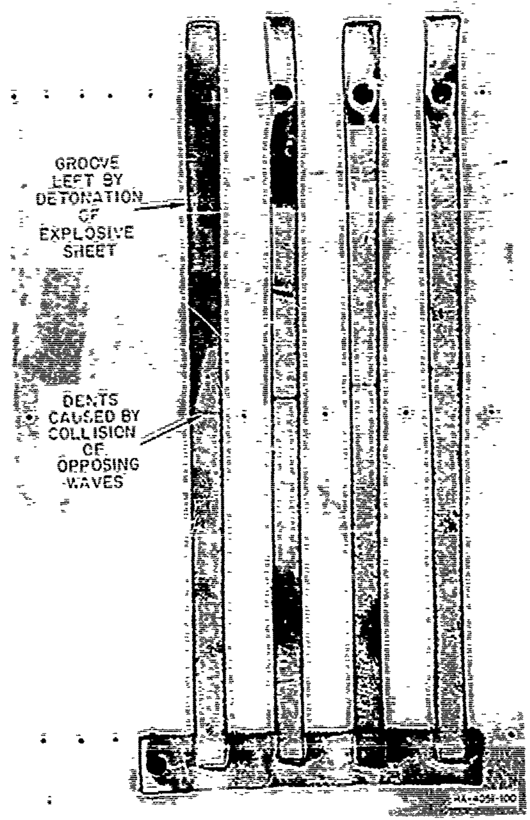


FIG. 3 TYPICAL TEST RESULT = WITNESS PLATE

For each shot a standard test cup is modified as shown in Fig. 4a and an aluminum witness plate prepared as in Fig. 4b.

Using a razor blade, five pieces of MDF, 20.00 inches long are cut on a piece of wood or Micarta. Five 1/2-inch-wide strips of sheet explosives are cut. One is about 4 inches long, the other 8.00 inches. Using precision scales and squares, the short strip is cemented parallel to the short edge of the plate with one end over the single hole. The long strips are cemented parallel to each other, one

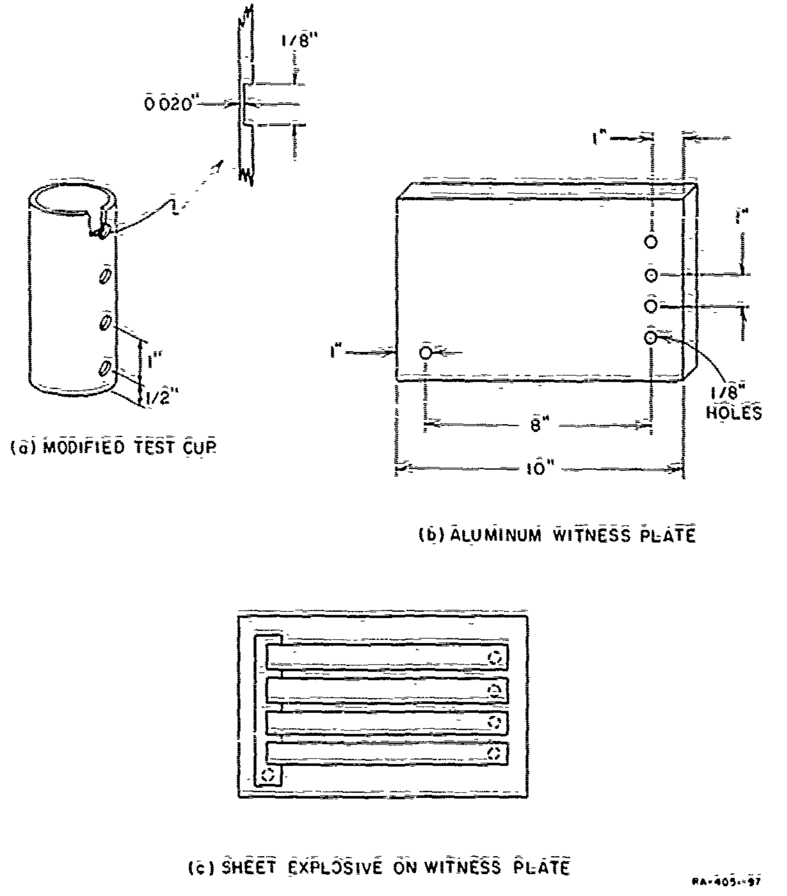
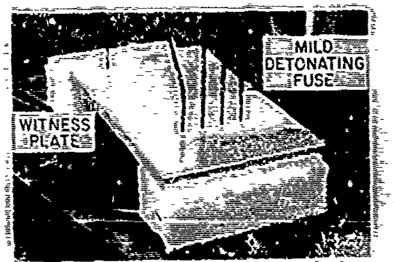


FIG. 4 TEST COMPONENTS

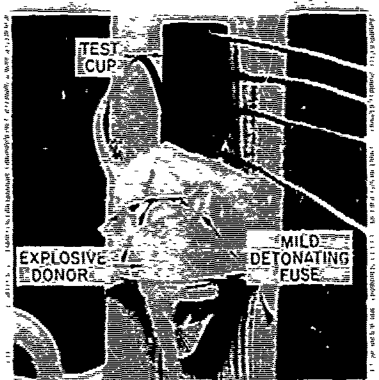
end over each of the remaining four holes and the other end over and in contact with the short strip (see Figs. 4c and 5a).

The test cup and booster are assembled in prescribed fashion and the witness plate secured nearby. One end of each of the 20 inch lengths of MDF is inserted through a hole in the plate until it contacts the explosive sheet (Fig. 5b). The other ends are put in place on the charge (no auxiliary booster is used) as shown schematically in Fig. 5c; four along the cup wall, one to the initiator. All ends are cemented securely in place.

(a) MDF, PLATE, AND SHEET EXPLOSIVE



(b) MDF AND WITNESS PLATE



(c) TEST CUP, BOOSTER AND MDF

FIG. 5 ASSEMBLED COMPONENTS

The results of a series of tests to evaluate the method are presented in Table III. Shots 1, 4, and 5 established a useful witness plate thickness: viz. 1/2 inch aluminum. Shots 2, 3, and 6 conducted with liquid nitromethane demonstrated that detonation of a liquid in the test cup would propagate through the walls to initiate the MDF and that the plate dents could be used to calculate a velocity.

A number of control experiments were conducted. Using sheet explosive to line the cup (Tests 4 and 5) or unconfined Composition B, (Test 11), it was again demonstrated that a stable high velocity could be detected reliably.

Tests 12 through 16 established that most reliable results were obtained using 20 grain per foot PETN, filled MDF, and Detasheet D-1 sheet explosive.

Table III

RESULTS OF EXPLOSIVE WITNESS SENSITIVITY TEST EVALUATION

Shot No.	Sample	Booster	Attenuator	Detonating Fuse	Explosive Sheet	Witness Plate	Shock Velocity (mm/μsec) 1	2	3	Remarks
1	None	None	None	MDF	0.030" Detasheet* D	1/4" Aluminum				Plate severed
2	Nitromethane 20°C	Tetryl (2 pellets)	None	20 grain PETN	506-D*	1/4" Aluminum	3.8	3.8	3.3	
3	Nitromethane 20°C	Tetryl (2 pellets)	None	20 grain PETN	506-D*	1/4" Aluminum	4.9	5.4	5.6	
4	506-D* lining cup	Tetryl (1 pellet)	None	20 grain PETN	506-D*	1/4" Aluminum	7.3			Plate severed at points of convergence
5	506-D* lining cup	Tetryl (1 pellet)	None	20 grain PETN	506-D*	1/2" Aluminum			6.1	#2 probe severed by fragment
6	Nitromethane 20°C	Tetryl (1 pellet)	None	23 grain PETN	506-D*	1/2" Aluminum	5.8	6.0	6.1	
7	Nitromethane 20°C	Tetryl (2 pellets)	40 cards	20 grain PETN	506-D*	1/2" Aluminum	4.9	7.1	6.3	
8	Nitromethane 20°C	Tetryl (2 pellets)	60 cards	30 grain PETN	506-D*	1/2" Aluminum	2.9	2.6		4th intercept off plate
9	Nitromethane 20°C	Tetryl (2 pellets)	50 cards	20 grain PETN	506-D*	1/2" Aluminum				No record obtained (Human error)
10	H_2O 20°C	Tetryl (1 pellet)	50 cards	20 grain PETN	506-D*	1/2" Aluminum	2.63			3rd and 4th intercepts off plate
11	Comp. B 20°C	Tetryl (1 pellet)	None	20 grain PETN	506-D*	1/2" Aluminum	6.9	7.9	7.1	Ideal velocity = 7.8 mm/μsec
12a	Nitromethane 20°C	Tetryl (2 pellets)	40 cards	20 grain PETN	506-D*	1/2" Aluminum	3.01	-	-	MDF functioned properly
12b	Nitromethane 20°C	Tetryl (2 pellets)	40 cards	20 grain RDX	506-D*	1/2" Aluminum	-	-	-	MDF did not initiate
13	Nitromethane 20°C	Tetryl (2 pellets)	40 cards	20 grain RDX	0.042" Deta Sheet* C-1	1/2" Aluminum				MDF did not initiate reliably
14	None	Tetryl (1 pellet)	None	10 and 20 grain PETN	0.042" Deta Sheet* D-1 (green)	1/2" Aluminum	-	-	-	MDF did not initiate reliably (attempted simultaneous initiation of each length of MDF)
15	None	Tetryl (1 pellet)	None	10 and 20 grain PETN	0.042" Deta Sheet* D-1 (red)	1/2" Aluminum				Initiated reliably
16	EL-506-D*	Tetryl (1 pellet)	None	20 grain PETN	0.042" Deta Sheet* D-1 (red)	1/2" Aluminum	Attempted simultaneous initiation			Reliable initiation accomplished
17	None	Tetryl (1 pellet)	None	20 grain RDX in liquid N_2 and at 20°C	0.042" Deta Sheet* D-1	1/2" Aluminum				Results reproducible but temperature dependent
18	None	Tetryl (1 pellet)	None	20 grain PETN in liquid N_2 and at 20°C	0.042" Deta Sheet* D-1	1/2" Aluminum				Results reproducible but temperature dependent
19	None	Tetryl (1 pellet)	None	20 grain PETN in liquid N_2 and at 20°C	0.042" Deta Sheet* D-1	1/2" Aluminum				Results reproducible but cold leg did not initiate
20	Nitromethane in liquid N_2	Tetryl (2 pellets)	None	20 grain PETN	0.042" Deta Sheet* D-1	1/2" Aluminum	Not analyzed yet			All points obtained - good record
21	Empty cup	Tetryl (2 pellets)	None	20 grain PETN	0.042" Deta Sheet* D-1	1/2" Aluminum				No. 1 intersection obtained. All others off plate

*Trade Mark E. I. duPont de Nemours and Company

A failing (i.e., nonpropagating) detonation wave, should be detected by a decelerating wave velocity rather than by failure of the MDF to detonate. Shots 7 and 8, conducted on either side of the sensitivity limit from nitromethane demonstrated that the explosive witness met this requirement. Thus, using 40 cards, nitromethane detonates as confirmed by the approximately constant high velocity calculated at each station. However, with 60 cards nitromethane does not propagate detonation as evidenced by the decreasing velocity recorded. This result can be compared with the results of shot No. 10 using water: the low velocity initially recorded decays rapidly so that no record is obtained at the third and fourth fingers. These measurements confirm that the test is a high-velocity sensor rather than a detonation sensor, the desired result.

Low temperature behavior was examined by shots 17 through 21, the performances of PETN and RDX MDF were found to be satisfactory in liquid nitrogen ($78^{o}K$) and a reasonable velocity record was obtained using nitromethane at the same temperature. Using an empty cup, shot 21 attested to the desirable absence of a shock in the cup wall strong enough to initiate the MDF.

C. Discussion

The modified Dautriche method described and tested functions reliably and is able to distinguish among the following situations:

1) Shock deceleration through a nonreactive material such as water (shot No. 10)

2) Shock deceleration and detonation failure in a reactive liquid (shot No. 8)

3) Shock and detonation propagation in explosive liquids or solids (shots No. 2-7, 9, 11-13, 16, 20, 22)

The following test components perform properly:

1) Test cup--as specified by the LPIA test--although at low temperatures leakage is a problem and thought is being

given to replacing the Teflon diaphragm with one of steel or other metal soldered to the cap.

2) MDF--20-inch lengths of 20 grain/foot PETN MDF

3) Sheet explosive--several are satisfactory including:
   a) 42-mil thick C-1 Detasheet
   b) 42-mil thick D-1 Detasheet (green)
   c) 42-mil thick D-1 Detasheet (red)

4) Witness plates--2024 aluminum 6 x 10 x 1/2 inches.

Although discrimination between stable and unstable detonation is reliable, calculated velocities are not as precise as anticipated. This may not be cause for serious concern as precise values are not a requirement.

D. Future Work

Experimental work planned for the coming quarter includes test of the continuous wire under similar conditions both alone and in conjunction with the explosive witness.

IV PHYSICS AND CHEMISTRY OF DETONATION

(Leslie B. Seely, Marjorie W. Evans, A. J. Bartlett, and D. Tegg)

A Failure Diameter of Difluoroamino Compounds

The failure diameter of liquid explosive--if it were large enough--could be of practical importance for the design of safe piping. Failure diameter is also of theoretical importance, since its magnitude is determined by competition between the chemical reaction rate and the flow divergence.[2] The results on 1,2-DP, 2,2-DP, and IBA in lead confinement are not quite complete, but the safety implications are evident: all three compounds will propagate in very small diameters in metal confinement.

The conditions used for test were chosen for theoretical simplicity. Lead was used[1] as the confining material because its sound velocity is very much lower than the detonation velocity of any of the three compounds; this simplifies the interaction at the explosive-wall interface. The lead was used in the form of blocks rather than tubing to give a very thick wall and avoid having to consider reverberations. These relatively large pieces of lead had the added advantage that they stayed in one piece under the disrupture force of the detonation, thus serving as their own witness blocks

Many of the difficulties in performing failure-diameter tests on liquids derive from properties that are quite general among homogeneous explosives but distinct from those of heterogeneous explosives For instance, failure diameter for liquids is anomalously large in glass confinement, and failure occurs by means of "dark waves."[3] The failure diameter of a liquid explosive in metal, even a metal of very

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[2] M. W. Evans, J. Chem. Phys. 36, 193 (1962).

[3] A. W. Campbell, T. E. Holland, M. E. Malin and T. P. Cotter, Jr., Nature 178, 38-9 (1956).

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low density, will be much smaller than in glass, and dark waves will not make their appearance except at discontinuities in the metal confinement These dark waves are not well understood Thus, if we are to use failure diameter data to gain information on chemical reaction processes, it seems clear that we must limit studies to cases where failure occurs not via dark waves but rather via smooth-flow divergence.

An ideal failure diameter test would involve a very long charge so that the test section could be considered to be boosted by an identical section preceding it. The size of the booster would then be of no importance provided it was large enough. In practice, the length of hole that can be satisfactorily fabricated is limited, and it is therefore of great importance to use the correct booster in order to save charge length. If the booster is too small the explosive will fail no matter how large the diameter; if very much too large, the explosive will shoot below failure diameter through the limited length available. The preferred situation is to overboost slightly. This overboosting is a guarantee against "strange waves," which are of safety interest, of course, but for which no satisfactory theory exists. However, failure diameters for weak waves are reported to be larger than for full-strength waves,[4] so we are justified from the point of view of both theory and safety in concerning ourselves with the failure diameter of strong waves.

For failure diameter tests, we would suppose that holes in a confining medium must be fabricated with precision, since irregularities are expected to produce failures. For instance, with nitromethane an abrupt increase in pipe diameter is used to prevent propagation of detonation through practical piping systems. For the compounds of interest here, the exact quality of surface required for holes in lead is not known. However, it was found that holes could be made in lead with a mirror-like finish so that there was no reason to accept any visible irregularities. The process of fabrication consisted in forcing a round-ended drill rod through the lead with a drill press. The flow of lead

[4]R. W. VanDolah, R. W. Watson, F. C. Gibson, and C. M. Mason, International Conference on Sensitivity (London, 1963), Session I, Article VI

around the rod during pressing apparently produced no density above the true density of lead, since there was no evidence of spring-back and the yield strength of lead is extremely low.

In Fig. 6 the sectioned 2-inch cube of lead shows the quality of the surface inside a 1/4-inch tube even though in this particular sample some oxidation took place before the photograph was taken. On the right is a similar unsectioned block after firing with 1,2-DP.

A 1 x 1 x 2 inch block containing a 1.59 mm hole is diagrammed in Fig 7 The bottom is closed with a Tedlar film 0.001 inch thick glued with epoxy cement. Care must be taken that the glue does not occlude the hole. The booster is a 3.1 x 3.1 mm pellet of RDX pressed to a density of 1.67 gm/cm^3. The detonator is a Dupont #311B. The tubes were carefully filled with liquid explosive by means of a micro-syringe before the booster was attached. It was then possible to inspect over a light for entrapped air

Shots were fired with 1,2-DP with a variety of booster strengths (minimum size was that specified for Fig 7) at 6 35 mm, 3 16 mm, 1 59 mm, 1.14 mm, and 0.81 mm diameters. No failure was encountered. Figure 8 shows sectioned billets from 1,2-DP firings with two sizes of booster at 0.81 mm diameter.

Only three shots were fired with 2,2-DP. All were at 0.81 mm diameter and all fired. The billets were indistinguishable from the corresponding 1,2-DP shots.

Fourteen shots were fired with IBA at 0.81 mm using two sizes of booster. Fifty percent failed, all of them within 10 diameters of the booster. Sectioned tubes are shown in Fig. 9.

We have concluded from these results that the failure diameter of IBA in lead is very close to 0.81 mm while the failure diameters for 1,2-DP and 2,2-DP lie some distance below that value. Just how far below depends somewhat on the interpretation put on the two expansion diameters seen clearly in most of the billets.

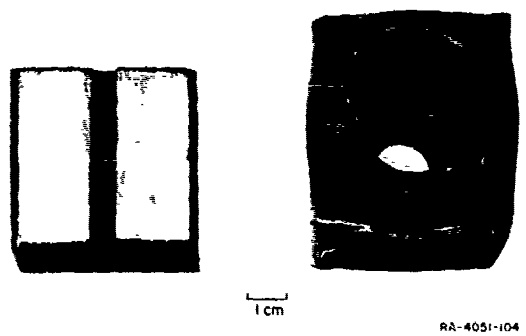

FIG. 6 TWO-INCH LEAD CUBE, ON THE LEFT SECTIONED TO SHOW THE INNER SURFACE OF A 1 4-INCH HOLE, ON THE RIGHT, A SIMILAR CUBE AFTER DETONATION OF 1, 2-DP

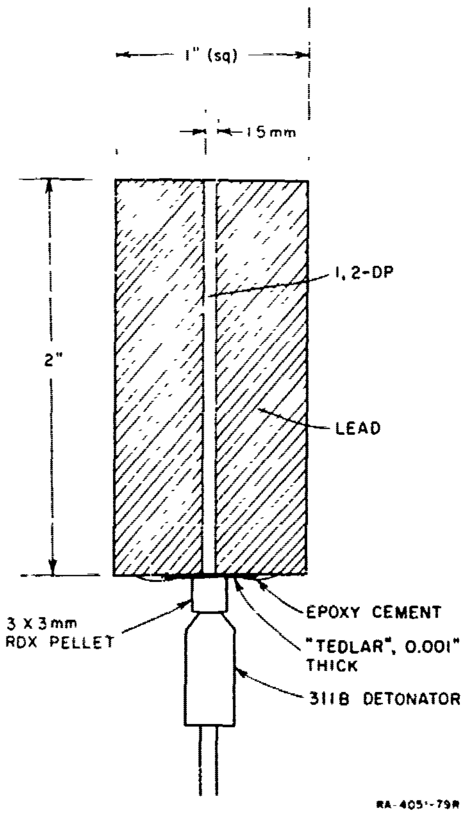

FIG. 7 DIAGRAM OF A 1.59 mm TEST LEAD BILLET READY FOR FIRING

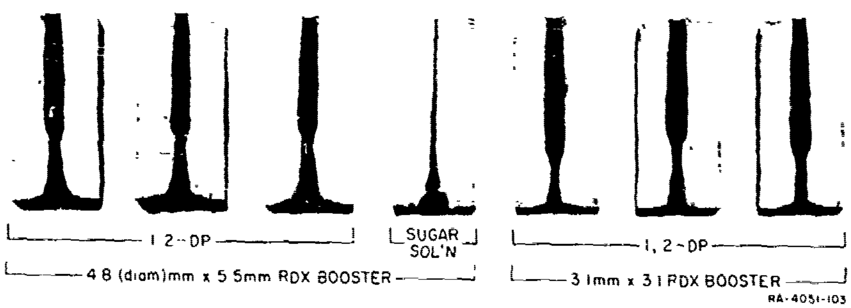

FIG. 8 LEAD BILLETS SECTIONED AFTER FIRING. The hole diameter was 0.81 mm, the explosive 1, 2-DP On the left the charges were boostered with 4.8 (diam) mm RDX at 1.67 g cm^{-3}. In the center the hole was filled with sugar solution - 1.26 g cm^{-3} instead of 1 2-DP On the right the RDX boosters were 3.1 mm 3.1 mm at 1.67 g cm^{-3}.

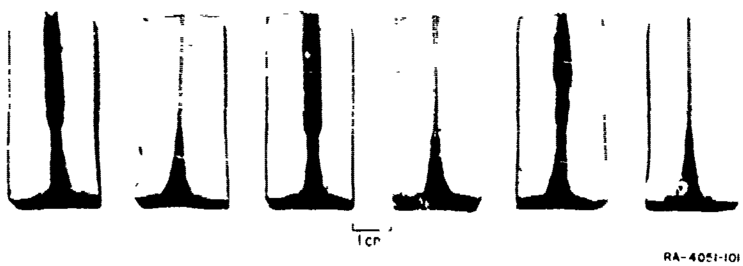

FIG. 9 SECTIONED 0.81 mm LEAD BILLETS AFTER IBA WAS FIRED WITH 3.1 mm · 3.1 mm RDX BOOSTERS. Failures were recorded for one half the shots.

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The existence of two expansion diameters might be a phenomenon of initiation with the detonation forming at the rear surface and overtaking the shock at the point indicated by the expansion. However, there are several facts that contradict such an interpretation. First, unless the pressure is held on the initiating surface, continued reaction there is unlikely. We would not expect initiation to take place by that mode in this geometry even though it has been observed in plane-wave experiments. Second, in homogeneous initiation the pressure in the region near the booster is supposed to be very high and to fall after the overdriven wave breaks through the shock front. Thus this sequence would not be expected to lead to the observed form of the expanded billets.

The distance that the "low-powered" wave travels in the lead before transition is fairly reproducible for a given booster and seems to depend on the size of the booster. In Fig. 10 are shown some billets fired with inadvertently weak composite boosters. Here the distance traveled before the transition varied, an effect due to the variable strength of the boosters. It will be noticed that in one case the wave never made the transition to "high order." Although the distance traveled was only 50 mm. it amounted to 64 charge diameters.

Tests are also being run on nitromethane so that we will have the method illustrated on a fairly well-known material. At present it can only be said that the failure diameter of nitromethane in lead lies somewhere between 1.6 and 3.2 mm.

B. Failure Diameters Predicted by Theory

The theory of failure diameter has been demonstrated for these particular compounds in Ref. 1. At that time the failure diameter, even in lead, was thought to be considerably larger than present experimental results demonstrate. In Fig. 11, corresponding to Fig. 36 of Ref. 1, the constants in the equation for the reaction rate constant are plotted, the logarithm of the kinetic frequency factor ν as ordinate, and the activation energy E_a as abscissa. The solid straight lines are for the indicated failure diameters and the broken lines are for the indicated shock sensitivities. Present information on the failure diameters and

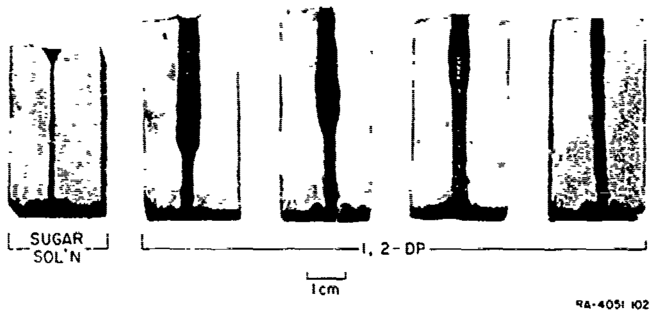

FIG. 10 SECTIONED 0.81 mm LEAD BILLETS AFTER 1, 2-DP WAS FIRED WITH COMPOSITE BOOSTERS WHOSE ACTION WAS SOMEWHAT WEAK AND IRREPRODUCIBLE. Attention is directed to the billet on the extreme right which shows that the wave traveled in the weak mode for 64 diameters.

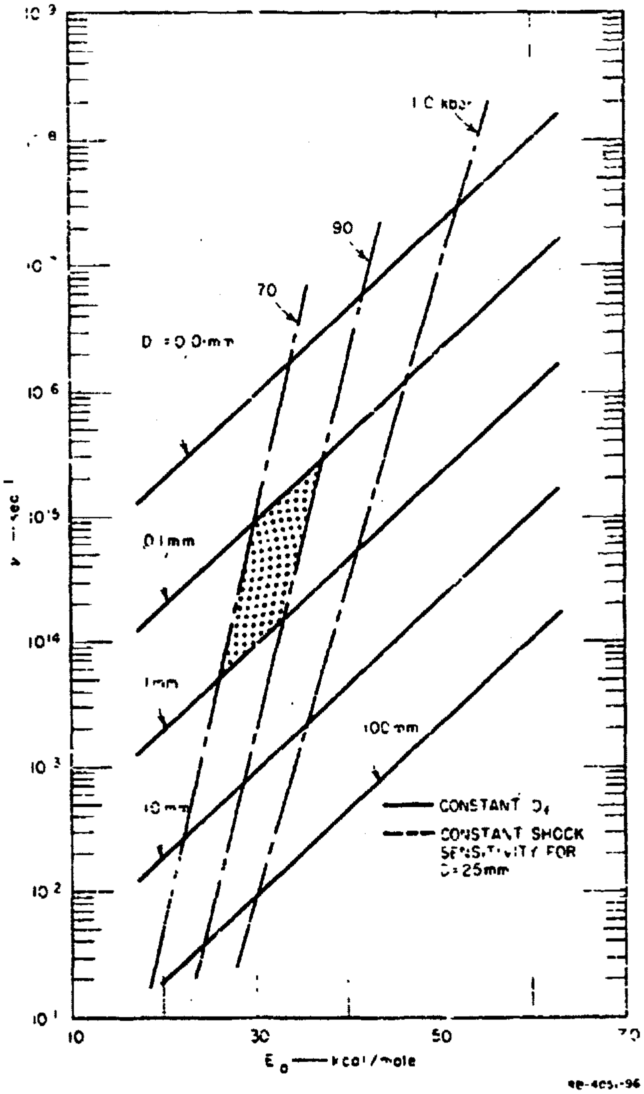

FIG. 11 KINETIC FREQUENCY FACTOR AND ACTIVATION ENERGY RELATED WITH FAILURE DIAMETER AND SHOCK SENSITIVITY

[illegible] shock sensitivity (see Section II) would place 1,2-DP, 2,2-DP and IPA within the shaded trapezoid. There is still so much doubt about the reaction kinetics and the diameter effect for these explosives that it is impossible to say that predictions of the theory are confirmed. However, the relationships between the various properties of the explosive have been defined, and as the data become more precise the adequacy of the theoretical assumptions can perhaps be assessed.

C. Future Work

Further work is planned on the failure diameter of nitromethane and IPA in lead. This will consist of tests near the failure diameter to define more clearly the statistical nature of the % fire-vs-diameter curve and to confirm that the correct booster size is being used. For 1,2-DP a measurement of the velocity of the slow wave will be made. An attempt will be made to determine the failure diameter of these explosives in another material of low sound velocity. Finally, special tests will be made to determine the expansion angle, first in lead and later in whatever other material proves satisfactory.

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THERMAL DECOMPOSITION OF NF COMPOUNDS

(Theodore Mill, David Ross, and Marilynne Smart)

A. Introduction

Previous work[4] has shown that the bis(difluoroamino)propane isomers and IBA undergo thermal decomposition by the elimination of HF. The elimination is markedly accelerated in the presence of acids (HF and HCl), neutral salts (KCl and KF), and even at room temperature by bases (pyridine and sodium butoxide). Surface effects which were noted in the thermal decomposition reactions may also play an important role in some of the reactions involving additives. In order to define the mechanistic features of the acid, base, and salt promoted reactions, we have begun an examination of HF elimination in homogeneous systems with 1,2-DP at or near room temperature.

B. Elimination of HF from 1,2-DP

1. Base Promoted Elimination

The decomposition was investigated in bases of various strengths. An immediate reaction resulted upon addition of 1,2-DP to 0.7 M sodium butoxide in n-BuOH. Titration for remaining base immediately after the addition showed that four equivalents (4.02 and 4.09 in two separate runs) of base were used per equivalent of NF compound. No products were identified. Upon acidification only water-soluble materials resulted.

The reaction of 1,2-DP with triethylamine at room temperature was studied (via vapor-phase chromatography) with nitrobenzene as solvent. In an equimolar mixture (0.2 M) of 1,2-DP and triethylamine, the NF compound slowly disappeared with simultaneous formation of 2-(N-fluoroimino) propionitrile (NFP). 1,2-DP completely disappeared in twenty hours. The imino compound, accounting for more than 80% of the starting material, was unchanged after several days and apparently stable under these conditions

Since three molecules of HF must be eliminated from the starting NF compound to form NFP, the fact that one equivalent of base gives a high yield of NFP must be explained. It is conceivable that the resulting triethylammonium hydrofluoride is itself involved in the elimination reaction. (As noted in the following section, neutral salts have been observed to catalyze the decomposition.) Alternatively, the intermediate imino-compounds I and/or II, formed through a single elimination, may easily undergo further HF elimination, either spontaneously or during vapor-phase chromatography, to give NFP. Neither of these intermediate compounds has been detected by g.l.c.

$$\underset{\text{I}}{CH_3 - \overset{\overset{NF}{\|}}{C} - CH_2NF_2} \qquad\qquad \underset{\text{II}}{CH_3 - \overset{\overset{NF_2}{|}}{CH} - CH = NF}$$

In another experiment, three equivalents of triethylamine were added to 1,2-DP (0.2 M) in nitrobenzene. All of the 1,2-DP disappeared immediately. The integrated areas of the chromatogram indicated that NFP was formed in 93% yield (yield based upon starting NF compound). Six percent of the 1,2-DP remained unreacted. A chromatogram taken twenty hours after initial mixing showed no NFP remained. No other volatile compounds were detected; apparently the iminonitrile reacts with triethylamine to yield nonvolatile materials. Sodium acetate in methanol (0.2 M), a much weaker base, effected a slower elimination and gave NFP which did not disappear on standing. The reaction of sodium acetate with 1,2-DP had a half-life of about 24 hours compared with less than a minute for an experiment with triethylamine at the same concentration of reactants.

2. Acid and Salt Catalyzed Elimination

Although both HCl and HF catalysis have been observed with 1,2-DP, the mechanism of this catalysis is by no means clear inasmuch as both KF and KCl also catalyze the decomposition heterogeneously. Experiments in methanol at 50° with 0.055 M 1,2-DP and 0.2 M HCl gave a tenfold increase in rate of disappearance of 1,2-DP compared to

a similar solution without acid. The same concentration of p-toluene-s[illegible] al. as effective. Lithium chloride gave rise to an acceleration similar to HCl, and $LiClO_4$ showed some acceleration. Since perchlorate ion is not nucleophilic, these results suggest that the catalysis observed here is associated in part with a medium effect and in part with anionic catalysis. The relatively slower reaction with the strong sulfonic acid tentatively indicates that acid catalysis is less important than either of the other effects. This conclusion is surprising in view of the observed and unique acid catalysis observed with alkyl and acyl fluorides.[5] Additional, quantitative experiments using CF_3COOH are planned.

C. Kinetics and Mechanism of Decomposition of 1,3-DP

1. Decomposition of 1,3-DP in Nitrobenzene

The rate of decomposition of 1,3-DP in nitrobenzene was studied over the temperature range 176-200°C. As in previous work, sealed glass capillary tubes lined with sodium fluoride were used as containers. These were held at the desired temperature for varying lengths of time, removed from the bath and cooled, and the contents analyzed by g.l.c. Difficulty was encountered in that the 1,3-DP decomposes on most suitable columns under operating conditions, including the didecylphthalate column used for the other NF compounds. However, fair reproducibility could be obtained with a DC-710 column.

If 1,3-DP decomposes by an HF elimination mechanism similar to that by which the other NF compounds decompose, an expected product would be malononitrile $CH_2(CN)_2$. A small amount of malononitrile is in fact formed and was identified by g.l.c. However, the major products were a very volatile component with an elution time similar to that for air, possibly HF, and a dark brown tarry component. This latter product has not been identified, but it is not malononitrile dimer, $CN-\underset{NC}{\underset{|}{CH}}=\underset{NH_2}{\underset{|}{C}}-CH_2-CN$, on the basis of the infrared spectrum.

[5] C. G. Swain and R. E. Spalding, J. Am. Chem. Soc., 82, 6104 (1960).

2. Decomposition in Gas Phase

1, 3-DP was decomposed at 190°C in a dried pyrex bulb at a pressure of 50 mm. At this temperature, the half-life was about 3-5 hrs. The bulb was then broken open under vacuum and the volatiles pumped off for analysis by mass spectrometry. The major gaseous products were 41.4% CO_2, 33.3% CO, 12.5% SiF_4, 4.2% N_2. This accounted for about 10% of the 1, 3-DP--the remainder having formed an adherent brown coating on the walls of the vessel. Elemental analysis of this brown solid gave: C, 16.47%, H, 3.86%; N, 17.3%; F, 41.3%; Ash, 1.27%. All the fluorine is ionic in character. Formulas calculated from analysis and adjusted to correspond to the original nitrogen ratio gives $C_{2.2}H_{6.2}N_{2.0}F_{3.0}$. This formula is short 0.8 C and 1.0 F, part of which were observed in the form of CO, CO_2, and SiF_4. The data indicate that the residue results from complete dehydrofluorination of 1, 3-DP, followed by cleavage of a cyano group, possibly after condensation and hydrolysis on the walls of the vessel.

3. Effect of Solvent and Possible Acid Catalysis

Various amounts of chloroacetic acid were added to solutions of 1, 3-DP (0.052 M) in both nitrobenzene and chlorobenzene. These were then thermostated at 176°C for 90 min. The results are shown in Table IV.

Catalysis observed in nitrobenzene may be due to chloroacetate ion rather than acid catalysis, the effect being analogous to the acetate ion catalyzed elimination observed with 1, 2-DP in methanol, discussed above. The striking difference in effectiveness of the acid in nitrobenzene and chlorobenzene is probably due to the greater degree of ionization of chloroacetic acid in nitrobenzene.

Reaction With Base. 1, 3-DP readily reacts with triethylamine, pyridine, and sodium butoxide. The major product, as in the case of the thermal decomposition, is a dark tar. Infrared spectra show that this tar is not malononitrile or its dimer. No volatile products in any quantity were detected by g.l.c.

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Table IV

DECOMPOSITION OF 1, 3-DP at 170° FOR 90 MIN
IN THE PRESENCE OF CHLOROACETIC ACID

Solvent	Concentration of Acid (mole/liter)	% 1, 3-DP Remaining
Nitrobenzene	0	90
Nitrobenzene	0.11	12
Nitrobenzene	0.42	0
Chlorobenzene	0	91
Chlorobenzene	0.1[illegible]	84
Chlorobenzene	0.3[illegible]	82
Chlorobenzene	0.60	81

D. Future Work

Investigation on the effect of acids and bases on the decomposition of 1, 2-DP will continue with possible extension to similar systems containing 2, 2-DP.

APPENDIX A

Adaptation of the JANAF Booster Test: Data Reduction

The equation for reducing the data from the witness plates is derived as follows:

Assume the following:

1. There is a small, finite, but reproducible time for a detonation to propagate across explosive interfaces. This is frequently referred to as an "induction time."
2. The time required for two detonations originating at a common point, and meeting at a point x, is the same for two corresponding paths.
3. The detonation velocity of explosives is a reproducible function of environment.

Our notation is as follows:

P = lengths of MDF, the subscript denotes the particular branch

P_o = length of MDF from tetryl booster that initiates the explosive on witness plate

V = detonation velocity of any P with corresponding subscript

V_s = wave velocity within sample

V_w = detonation velocity of standard explosive used

L = distance between opposing points of initiation for each sheet explosive finger

x = point at which detonations meet: measured from MDF

ds' = distances between MDF on sample cup

dw' = distances between corresponding strips of explosive on witness plate

ds = distance from tetryl pellet to first MDF

dw = distance from the start to strip 1 on witness plate

μ, η = small, unknown, but reproducible delay or induction times in transition from cup to MDF and MDF to EL-506-D.

The time required for the detonation to travel from the tetryl through the sample cup, the first "finger" of MDF and to point x_1 in the sheet explosive is:

$$t_1 = \frac{ds}{V_s} + \mu + \frac{P_1}{V_1} + \eta + \frac{x_1}{V_w} \tag{1}$$

The time required for the detonation to travel from the tetryl through the "start" branch of the MDF and to x_1 through the sheet explosive from the opposite direction is:

$$t_1' = \frac{P_o}{V_o} + \eta + \frac{dw}{V_w} + \frac{L - x_1}{V_w} \tag{2}$$

Equating (1) and (2) and rearranging terms:

$$\frac{ds}{V_s} = \frac{P_o}{V_o} - \frac{P_1}{V_1} + \frac{dw}{V_w} + \frac{L - 2x}{V_w} - \mu \tag{3}$$

Similarly, by equating the times of travel from the tetryl to point x_2 in the second finger of sheet explosive:

$$\frac{ds + ds'}{V_s} = \frac{P_o}{V_o} - \frac{P_2}{V_2} + \frac{dw + dw'}{V_w} + \frac{L - 2x_2}{V_w} - \mu \tag{4}$$

Subtracting (3) from (4) and noting that $P_1 = P_2$ and $V_1 = V_2$:

$$\frac{V_s}{V_w} = \frac{ds'}{dw' + 2\,(x_1 - x_2)} \tag{5}$$

V_w, ds', dw' are conditions of the experiment; x_1 and x_2 are measured; therefore V_s can be calculated.